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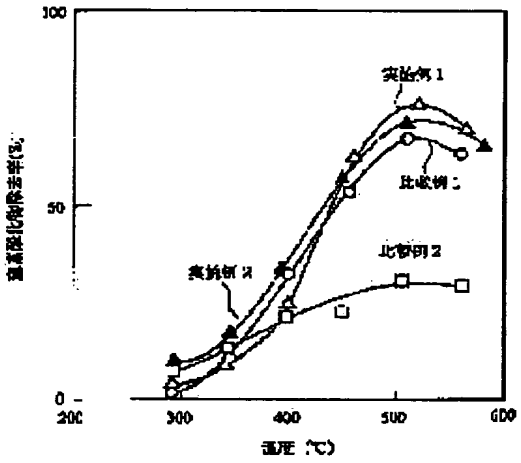
(54) CATALYST FOR REMOVING NITROGEN OXIDES AND METHOD OF REMOVING THE SAME

(57)Abstract:
PURPOSE: To provide a catalyst for removing nitrogen oxides and a method using it where nitrogen oxides are effectively removed from waste combustion gas contg. oxygen whose amount is not less than the theoretical reaction one to the unburnt content of nitrogen oxides, carbon monoxide, hydrocarbon, etc.
CONSTITUTION: A catalyst for removing nitrogen oxides which (a) silver or silver oxide by 0.2-15wt.% (expressed in terms of silver element) and (b) at least one metal element selected from a group consisting of alkaline metal elements and alkaline earth metals by ≤50wt.% of the carried quantity of silver components (expressed in terms of silver element) are deposited on 100wt.% of porous inorganic oxide to form is installed in mid-way of a waste gas conduit tube. And hydrocarbon or oxygen contg. organic compounds not more than five times the weight of nitrogen oxide in waste gas are added on tie upstream side of the catalyst and the waste gas comes into contact with the catalyst at 200-600°C, causing nitrogen oxides to be removed by the reaction with hydrocarbon.



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CLAIMS

[Claim(s)]
[Claim 1] It is the catalyst which removes nitrogen oxides from the combustion gas containing nitrogen oxides and more oxygen than the theoretical reacting weight to the non-burned component which lives together. In 100 % of the weight of porous inorganic oxides, it is (a). Silver or a silver oxide 0.2 - 15 % of the weight (silver element reduced property), (b) The amount of silver component support comes at least to carry out support of a kind of metallic element chosen from the group which consists of alkali metals and alkaline earth metal 50 or less (metallic element reduced property) % of the weight. It is alike, install and 5 or less times [of nitrogen-oxides weight] the hydrocarbon or oxygenated organic compound in said exhaust gas is added by the upstream of said catalyst. said catalyst -- exhaust gas -- a conduit -- on the way -- The nitrogen-oxides removal catalyst characterized by for exhaust gas contacting and having in said catalyst in 200-600 degrees C, and removing said nitrogen oxides by the reaction with said hydrocarbon or an oxygenated organic compound.
[Claim 2] The nitrogen-oxides removal catalyst characterized by the inorganic oxide of said porosity being an alumina or an alumina system multiple oxide in a catalyst according to claim 1.
[Claim 3] In the approach of removing nitrogen oxides from the combustion gas containing nitrogen oxides and more oxygen than the theoretical reacting weight to the non-burned component which lives together In 100 % of the weight of porous inorganic oxides, it is (a). Silver or a silver oxide 0.2 - 15 % of the weight (silver element reduced property), (b) It is alike and installs. the catalyst to which the amount of silver component support comes at least to carry out support of a kind of metallic element chosen from the group which consists of alkali metals and alkaline earth metal 50 or less (metallic element reduced property) % of the weight -- exhaust gas -- a conduit -- on the way -- To the upstream of said catalyst, 5 or less times [of nitrogen-oxides weight] the hydrocarbon or oxygenated organic compound in said exhaust gas is added. The approach characterized by contacting exhaust gas for said catalyst, having it in 200-600 degrees C, making said nitrogen oxides and said hydrocarbon, or an oxygenated organic compound react, and removing said nitrogen oxides.
[Claim 4] In the approach of removing nitrogen oxides from the combustion gas containing nitrogen oxides and more oxygen than the theoretical reacting weight to the non-burned component which lives together In 100 % of the weight of porous inorganic oxides, it is (a). Silver or a silver oxide 0.2 - 15 % of the weight (silver element reduced property), (b) It is alike and installs. the catalyst to which the amount of silver component support comes at least to carry out support of a kind of metallic element chosen from the group which consists of alkali metals and alkaline earth metal 50 or less (metallic element reduced property) % of the weight -- exhaust gas -- a conduit -- on the way -- The approach characterized by contacting exhaust gas for said catalyst, having it in 200-600 degrees C, making said nitrogen oxides and lipobiolite-ized hydrogen in said exhaust gas react, and removing said nitrogen oxides.

[Translation done.]

* NOTICES *

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application] This invention relates to the nitrogen-oxides removal catalyst and the removal approach the combustion gas containing superfluous oxygen to nitrogen oxides and nitrogen oxides are effectively removable.
[0002]
[Description of the Prior Art] In various kinds of combustion gases discharged from internal combustion engines, such as car motor, the burning appliance installed in works etc., a home fan heater, etc., nitrogen oxides (generally referred to as NOx), such as a nitrogen monoxide and a nitrogen dioxide, are contained with superfluous oxygen. Here, nitrogen oxides (NOx) point out a nitrogen monoxide and/or a nitrogen dioxide, and mean that more oxygen than the amount of theoretical oxygen required to burn non-burned components, such as a carbon monoxide contained in the exhaust gas, hydrogen, and a hydrocarbon, "including superfluous oxygen" is included.
[0003] These nitrogen oxides are set to one of the causes of acid rain, and pose a big problem on an environment. Therefore, various methods of removing the nitrogen oxides in the exhaust gas which various burning appliances discharge are examined.
[0004] As an approach of removing nitrogen oxides from the combustion gas containing superfluous oxygen, the selective contact reduction method using ammonia is especially put in practical use to large-scale fixed burners (large-sized combustion machines, such as works etc.).
[0005] However, in this approach, the ammonia used as a reducing agent of nitrogen oxides being expensive and ammonia have troubles, like that an ammonia injection rate must be controlled and generally equipment becomes large-sized, measuring the nitrogen-oxides concentration in exhaust gas so that having, therefore unreacted ammonia may not discharge toxicity.
[0006] Moreover, although there is a non-selective contact reduction method which returns nitrogen oxides as another approach, using gas, such as hydrogen, a carbon monoxide, and a hydrocarbon, as a reducing agent, by this approach, in order to perform reduction removal of effective nitrogen oxides, the reducing agent more than theoretical reacting weight with the oxygen in exhaust gas must be added, and there is a fault which consumes a reducing agent so much. For this reason, a non-selective contact reduction method becomes effective in practice only to the low exhaust gas of the residual oxygen density which burned near theoretical air fuel ratio, and is not deficiently practical to versatility.
[0007] Then, the method of adding the reducing agent below theoretical reacting weight with the oxygen in exhaust gas, and removing nitrogen oxides was proposed using the catalyst which supported transition metals to a zeolite or it. for example, JP,63-100919,A -- said -- 63-283727 number -- JP,1-130735,A and the 59th spring annual convention of the Chemical Society of Japan (1990) Two A526, this 60th autumn annual convention (1990) 3L420, 3L422, 3L423, "catalyst" vol.33 No.2, 59 pages, 1991, etc.
[0008] However, by these approaches, although nitrogen oxides were removable at high effectiveness to simulation exhaust gas which does not contain moisture, since moisture was contained about 10% in actual exhaust gas, it turned out that the elimination factor of nitrogen oxides falls remarkably.
[0009] Therefore, the purpose of this invention is offering the approach using the nitrogen-oxides catalyst and it which can remove nitrogen oxides from the combustion gas containing the oxygen more than the theoretical reacting weight to parts for un-burning, such as nitrogen oxides, a carbon monoxide, and a hydrocarbon, efficiently like the combustion gas from the gasoline engine which burns on a fixed burner and hyperoxia conditions, a diesel power plant, etc.
[0010]

[Means for Solving the Problem] In view of the above-mentioned technical problem, this invention person is (a) of the amount of specification to a porous inorganic oxide wholeheartedly about the exhaust gas which added the hydrocarbon or oxygenated organic compound of an amount corresponding to the amount of the nitrogen oxides contained in exhaust gas as a result of research. Silver or a silver oxide, and (b) When making the catalyst which comes to support alkali metal or alkaline earth metal contact at specific temperature, it discovered that nitrogen oxides were effectively removable, and this invention was completed.

[0011] Namely, the catalyst of this invention which removes nitrogen oxides from the combustion gas containing nitrogen oxides and more oxygen than the theoretical reacting weight to the non-burned component which lives together In 100 % of the weight of porous inorganic oxides, it is (a). Silver or a silver oxide 0.2 - 15 % of the weight (silver element reduced property), (b) The amount of silver component support comes at least to carry out support of a kind of metallic element chosen from the group which consists of alkali metals and alkaline earth metal 50 or less (metallic element reduced property) % of the weight. It is alike, install and 5 or less times [of nitrogen-oxides weight] the hydrocarbon or oxygenated organic compound in said exhaust gas is added by the upstream of said catalyst. said catalyst -- exhaust gas -- a conduit -- on the way -- It is characterized by for exhaust gas contacting and having in said catalyst in 200-600 degrees C, and removing said nitrogen oxides by the reaction with said hydrocarbon or an oxygenated organic compound.

[0012] Moreover, the primary method of this invention which removes nitrogen oxides from the combustion gas containing nitrogen oxides and more oxygen than the theoretical reacting weight to the non-burned component which lives together In 100 % of the weight of porous inorganic oxides, it is (a). Silver or a silver oxide 0.2 - 15 % of the weight (silver element reduced property), (b) It is alike and installs. the catalyst to which the amount of silver component support comes at least to carry out support of a kind of metallic element chosen from the group which consists of alkali metals and alkaline earth metal 50 or less (metallic element reduced property) % of the weight -- exhaust gas -- a conduit -- on the way -- To the upstream of said catalyst, 5 or less times [of nitrogen-oxides weight] the hydrocarbon or oxygenated organic compound in said exhaust gas is added. It is characterized by contacting exhaust gas for said catalyst, having it in 200-600 degrees C, making said nitrogen oxides and said hydrocarbon, or an oxygenated organic compound react, and removing said nitrogen oxides.

[0013] Furthermore, the second approach of this invention of removing nitrogen oxides from the combustion gas containing nitrogen oxides and more oxygen than the theoretical reacting weight to the non-burned component which lives together In 100 % of the weight of porous inorganic oxides, it is (a). Silver or a silver oxide 0.2 - 15 % of the weight (silver element reduced property), (b) It is alike and installs. the catalyst to which the amount of silver component support comes at least to carry out support of a kind of metallic element chosen from the group which consists of alkali metals and alkaline earth metal 50 or less (metallic element reduced property) % of the weight -- exhaust gas -- a conduit -- on the way -- It is characterized by contacting exhaust gas for said catalyst, having it in 200-600 degrees C, making said nitrogen oxides and lipobiolite-ized hydrogen in said exhaust gas react, and removing said nitrogen oxides.

[0014] Hereafter, this invention is explained to a detail. The catalyst used by this invention is (a) to a porous inorganic oxide. Silver or a silver oxide, and (b) It comes at least to support a kind of metallic element chosen from the group which consists of alkali metals and alkaline earth metal.

[0015] First, as a porous inorganic oxide, although a porous alumina, a titania, zirconias, those multiple oxides, etc. can be used, gamma-alumina or an alumina system multiple oxide is used preferably.

[0016] As for the specific surface area of a porous inorganic oxide, it is desirable that they are more than 30m2 / g. The touch area of exhaust gas and an inorganic oxide becomes it small that specific surface area is under 30m2 / g, and good nitrogen oxides cannot be removed. More desirable specific surface area of a porosity inorganic oxide is carried out to more than 80m2 / g. More than 100m2 / g are especially desirable.

[0017] Although silver or a silver oxide, and alkali metal and alkaline earth metal are supported by inorganic oxides, such as gamma-alumina, so that it may mention later, this inorganic oxide can be used in the condition, such as the shape of the shape of a pellet type, powder, and a honeycomb, and form, and tabular. Moreover, the coat of the porosity inorganic oxide which supported active species can be carried out to the base of the shape of the shape of HAMUNIKA which consists of components, such as heat-resistant cordierite and a mullite, and form, and it can also be used for it. The desirable gestalt of the catalyst of this invention carries out the coat of the catalyst to the base front face of the product made from the ceramics, or metal, and uses it for it. The gestalt of the catalyst of this invention desirable [one more] supports and uses a catalytic activity kind for the porosity inorganic oxide of a pellet type.

[0018] What supported with this invention at least a kind of metallic element chosen from the group which becomes inorganic oxides, such as gamma-alumina mentioned above, from (a) silver or a silver oxide, and (b) alkali metals and alkaline earth metal is used as a catalyst. The amount of support of silver or a silver oxide is an inorganic oxide although it changes with the gas hydrocarbon added in exhaust gas or the class of oxygenated organic compound, contact time with exhaust gas, etc. somewhat 100 It considers as weight % and may be the 0.2 - 15 % of the weight (silver element reduced property). 0.2 It is NOx even if it supports under with weight % the silver or the silver oxide of an amount which the effectiveness by support of silver or a silver oxide does not become remarkable, and exceeds 15 % of the weight. The improvement in the removal engine performance is not found. The amount of support of desirable silver or a silver oxide is 0.5 - 10 % of the weight. In addition, in the temperature field of exhaust gas, the silver supported by the inorganic oxide is in the condition of a metal or an oxide, and can be changed mutually easily.
[0019] As an alkali metal, it is desirable to use caesium, sodium, a potassium, etc. Moreover, as an alkaline earth metal, it is desirable to use calcium, strontium, and barium.
[0020] The amount of sum total support of alkali metals and alkaline earth metal is a silver component 100 It considers as weight % and may be 50 or less (element reduced property) % of the weight. If the amount of support exceeds 50% of the weight of a silver component, the removal effectiveness by the silver component will fall greatly. In addition, it is the lower limit of the amount of support 0.001 Considering as weight % is desirable. In addition, the above-mentioned metal exists in the state of an oxide in the temperature field of exhaust gas.
[0021] Well-known dip coating etc. can be used for inorganic oxides, such as gamma-alumina, as an approach of supporting silver, alkali metals, and alkaline earth metal. It is desirable in that case for a porous inorganic oxide to be immersed in a nitrate water solution etc., and to carry out a temperature up gradually at 100-600 degrees C, and to calcinate after desiccation, at about 70 degrees C. It is desirable to perform baking under an oxygen ambient atmosphere, nitrogen-gas-atmosphere mind, and a hydrogen gas stream. Finally in the case where it carries out under nitrogen-gas-atmosphere mind and a hydrogen gas stream, oxidation treatment is performed. This prevents silver sintering and the fall of the purification property of nitrogen oxides is prevented.
[0022] Next, the approach of this invention is explained. In exhaust gas, ethylene, a propylene, etc. are contained to some extent as lipobiolite-ized hydrogen. To not be enough for lipobiolite-ized hydrogen to return the nitrogen oxides in exhaust gas, it is necessary to add an organic compound from the exterior. the catalyst mentioned above at this time -- exhaust gas -- a conduit -- on the way -- it is alike, and installs and a hydrocarbon or an oxygenated organic compound is added in exhaust gas by the upstream of the installation part of a catalyst.
[0023] As a hydrocarbon, an alkane, an alkene, an alkyne, kerosene, gas oil, etc. are used. Preferably, liquefied hydrocarbons, such as acetylene, and a with a carbon numbers of three or more alkene (for example, propylene), kerosene, gas oil, etc. are used. As an oxygenated organic compound, it is desirable to use alcohols, such as ethanol.
[0024] The amount of the hydrocarbon added in exhaust gas or an oxygenated organic compound is made into 5 or less times of the weight of the nitrogen oxides in exhaust gas. When 5 times are exceeded, possibility that an additive will become superfluous in many cases and an unreacted hydrocarbon or an oxygenated organic compound will remain into exhaust gas is high. An addition is preferably made into 3 or less times of the amount of nitrogen oxides. In addition, a certain amount of [having also used the catalyst mentioned above, since hydrocarbons, such as an alkane, an alkene, and an alkyne, existed somewhat as a part for un-burning in exhaust gas] (even if it does not add a hydrocarbon) NOx The reduction effectiveness is seen.
[0025] Moreover, in this invention, the temperature of the exhaust gas in a catalyst installation part is kept at 200-600 degrees C. The reaction of an additive and nitrogen oxides does not advance that the temperature of exhaust gas is less than 200 degrees C, and good nitrogen oxides cannot be removed. On the other hand, if it is the temperature which exceeds 600 degrees C, the organic substance added will burn and the reduction removal property of nitrogen oxides will fall greatly.
[0026] Generally, if contact time becomes short, the removal property of nitrogen oxides will fall. Therefore, if it is desirable to support the amount of support of a catalytic activity kind, and to support many [and] amounts of support of a catalytic activity kind fewer when contact time is long and it does in this way when contact time is short, the reaction of a hydrocarbon and nitrogen oxides can be advanced efficiently. It is desirable to make the contact time which contacts exhaust gas for the above-mentioned catalyst more than 0.006 second and g/ml with the catalyst in this invention. Here, contact time expresses the time amount

(second) in contact with the catalyst 1ml (however, volume converted into reference condition) of whose exhaust gas containing a hydrocarbon is 1g. Desirable contact time is made more than 0.007 second and g/ml.
[0027]
[Example] The following concrete examples explain this invention to a detail further.
Porosity gamma-alumina of the pellet type of example 1 marketing (the diameter of 1.5mm respectively) Under the nitrogen air current which is immersed in the mixed water solution of a silver nitrate and a potassium nitrate in die length of about 6mm, and specific-surface-area 200 m2/g10g, and contains the hydrogen of 5 capacity % after desiccation at 70 degrees C It calcinated for 2 hours, respectively at each temperature of 150 degrees C, 200 degrees C, 300 degrees C, 400 degrees C, 500 degrees C, and 600 degrees C, and 2 % of the weight (element reduced property) of silver and 0.5 % of the weight (element reduced property) of potassiums were supported to pellet type gamma-alumina.
[0028] Next, 3.6g of acquired catalysts was installed within the reaction, the gas (a nitrogen monoxide, oxygen, a propylene, and nitrogen) of the presentation shown in Table 1 was passed by the flow rate of 4.4l./m (reference condition) (at this time, space velocity was 30000 h-1 and contact time was 0.05-second and g/ml), the exhaust gas temperature within a reaction was maintained at the range of 300-600 degrees C, and a propylene and nitrogen oxides were made to react.
[0029] The concentration of the nitrogen oxides in the gas after coil passage was measured with the chemiluminescence type nitrogen-oxides analyzer, and it asked for the elimination factor of nitrogen oxides. A result is shown in drawing 1 .
[0030] Table 1 component Concentration nitrogen monoxide 800 ppm oxygen 10 Capacity % propylene 1714 ppm nitrogen Remainder [0031] The coat of the 1.3g of the catalysts which supported 2 % of the weight (element reduced property) of silver and 0.5 % of the weight (element reduced property) of potassiums with the same approach as example 2 example 1 to powdered gamma-alumina (mean particle diameter of 40 micrometers, specific surface area of 200m 2 / g) was carried out to the commercial honeycomb Plastic solid made from cordierite (the diameter of 30mm, die length of 12.5mm) by the wash coat method. Using the Plastic solid which carried out the coat of this catalyst, it is the same conditions (space velocity is 30000h-1) as an example 1, and the removal trial of nitrogen oxides was performed. A test result is shown in drawing 1 .
[0032] Only silver was supported with the same approach as example of comparison 1 example 1 2% of the weight on the gamma-alumina pellet, and it considered as the catalyst by it. The removal trial of nitrogen oxides was performed like the example 1 using this catalyst except having maintained the exhaust gas temperature within a reaction at the range of 300-600 degrees C. A test result is shown in drawing 1 .
[0033] 2% of the weight, Ce was supported with the same approach as example of comparison 2 example 1 0.5% of the weight on the gamma-alumina pellet, and silver was made into the catalyst by it at it. The removal trial of nitrogen oxides was performed like the example 1 using this catalyst. A result is shown in drawing 1 .
[0034] As mentioned above, especially in examples 1 and 2, good removal of nitrogen oxides was seen at the exhaust gas temperature of 400-600 degrees C so that it might understand. On the other hand, if the catalyst of only the silver component which does not support alkali metal is used (example 1 of a comparison), the elimination factor of 500-degree C nitrogen oxides will become low. Moreover, in the catalyst (example 2 of a comparison) which supported the silver component and the rare earth metal, removal of high nitrogen oxides was not obtained by total-temperature within the limits.
[0035]
[Effect of the Invention] As explained in full detail above, according to the catalyst and approach of this invention, the nitrogen oxides in the exhaust gas containing superfluous oxygen are efficiently removable. Removal temperature (exhaust gas temperature) of nitrogen oxides can also be performed at low temperature as compared with about 500 degrees C or less and the old removal approach.
[0036] The nitrogen-oxides removal catalyst and approach of this invention are widely applicable to removal of the nitrogen oxides contained in exhaust gas, such as various combustion machines and an automobile.

[Translation done.]

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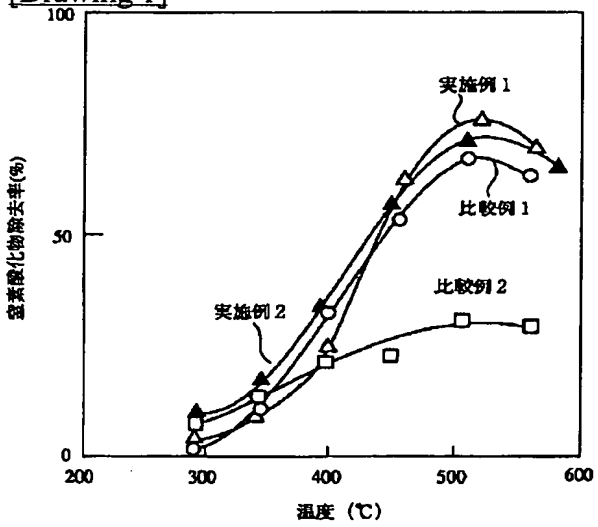
DRAWINGS

[Drawing 1]



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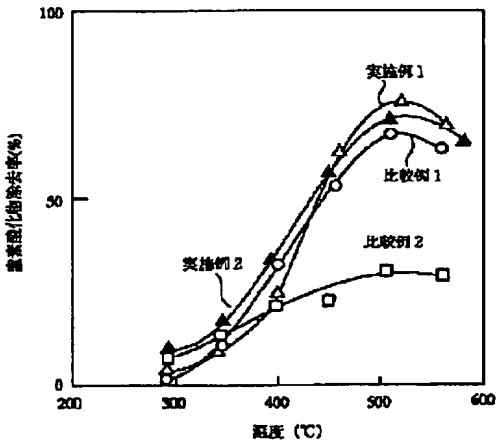

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(54)【発明の名称】　窒素酸化物除去触媒及び除去方法

(57)【要約】

【目的】　窒素酸化物、一酸化炭素、炭化水素等の未燃焼分に対する理論反応量以上の酸素を含有する燃焼排ガスから、効率良く窒素酸化物を除去することができる窒素酸化物除去触媒及びそれを用いた方法を提供する。

【構成】　多孔質の無機酸化物１００重量％に、(a) 銀又は銀酸化物を０．２～１５重量％（銀元素換算値）と、(b) アルカリ金属元素とアルカリ土類金属とからなる群より選ばれた少なくとも一種の金属元素を銀成分担持量の５０重量％以下（金属元素換算値）担持してなる窒素酸化物除去触媒であって、前記触媒を排ガス導管の途中に設置し、触媒の上流側で排ガス中の窒素酸化物重量の５倍以下の炭化水素又は含酸素有機化合物を添加し、２００～６００℃において排ガスが触媒に接触し、もって、前記炭化水素との反応により窒素酸化物を除去する。

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【特許請求の範囲】

【請求項１】　窒素酸化物と、共存する未燃焼成分に対する理論反応量より多い酸素とを含む燃焼排ガスから窒素酸化物を除去する触媒であって、多孔質の無機酸化物１００重量％に、(a) 銀又は銀酸化物を０．２～１５重量％（銀元素換算値）と、(b) アルカリ金属元素とアルカリ土類金属とからなる群より選ばれた少なくとも一種の金属元素を銀成分担持量の５０重量％以下（金属元素換算値）担持してなり、前記触媒を排ガス導管の途中に設置し、前記触媒の上流側で前記排ガス中の窒素酸化物重量の５倍以下の炭化水素又は含酸素有機化合物を添加し、２００～６００℃において排ガスが前記触媒に接触し、もって、前記炭化水素又は含酸素有機化合物との反応により前記窒素酸化物を除去することを特徴とする窒素酸化物除去触媒。

【請求項２】　請求項１に記載の触媒において、前記多孔質の無機酸化物がアルミナ又はアルミナ系複合酸化物であることを特徴とする窒素酸化物除去触媒。

【請求項３】　窒素酸化物と、共存する未燃焼成分に対する理論反応量より多い酸素とを含む燃焼排ガスから窒素酸化物を除去する方法において、多孔質の無機酸化物１００重量％に、(a) 銀又は銀酸化物を０．２～１５重量％（銀元素換算値）と、(b) アルカリ金属元素とアルカリ土類金属とからなる群より選ばれた少なくとも一種の金属元素を銀成分担持量の５０重量％以下（金属元素換算値）担持してなる触媒を排ガス導管の途中に設置し、前記触媒の上流側に、前記排ガス中の窒素酸化物重量の５倍以下の炭化水素又は含酸素有機化合物を添加し、２００～６００℃において排ガスを前記触媒に接触させ、もって、前記窒素酸化物と前記炭化水素又は含酸素有機化合物とを反応させて前記窒素酸化物を除去することを特徴とする方法。

【請求項４】　窒素酸化物と、共存する未燃焼成分に対する理論反応量より多い酸素とを含む燃焼排ガスから窒素酸化物を除去する方法において、多孔質の無機酸化物１００重量％に、(a) 銀又は銀酸化物を０．２～１５重量％（銀元素換算値）と、(b) アルカリ金属元素とアルカリ土類金属とからなる群より選ばれた少なくとも一種の金属元素を銀成分担持量の５０重量％以下（金属元素換算値）担持してなる触媒を排ガス導管の途中に設置し、２００～６００℃において排ガスを前記触媒に接触させ、もって、前記窒素酸化物と前記排ガス中の残留炭化水素とを反応させて前記窒素酸化物を除去することを特徴とする方法。

【発明の詳細な説明】

【０００１】

【産業上の利用分野】本発明は窒素酸化物と過剰の酸素を含む燃焼排ガスから、窒素酸化物を効果的に除去することのできる窒素酸化物除去触媒及び除去方法に関する。

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【０００２】

【従来の技術及び発明が解決しようとする課題】自動車用エンジン等の内燃機関や、工場等に設置された燃焼機器、家庭用ファンヒーターなどから排出される各種の燃焼排ガス中には、過剰の酸素とともに一酸化窒素、二酸化窒素等の窒素酸化物（一般にNOx と呼ばれる）が含まれている。ここで、窒素酸化物（NOx ）とは一酸化窒素及び／又は二酸化窒素を指し、「過剰の酸素を含む」とは、その排ガス中に含まれる一酸化炭素、水素、炭化水素等の未燃焼成分を燃焼するのに必要な理論酸素量より多い酸素を含むことを意味する。

【０００３】この窒素酸化物は酸性雨の原因の一つとされ、環境上の大きな問題となっている。そのため各種燃焼機器が排出する排ガス中の窒素酸化物を除去するさまざまな方法が検討されている。

【０００４】過剰の酸素を含む燃焼排ガスから窒素酸化物を除去する方法として、特に大規模な固定燃焼装置（工場等の大型燃焼機等）に対しては、アンモニアを用いる選択的接触還元法が実用化されている。

【０００５】しかしながら、この方法においては、窒素酸化物の還元剤として用いるアンモニアが高価であること、またアンモニアは毒性を有すること、そのために未反応のアンモニアが排出しないように排ガス中の窒素酸化物濃度を計測しながらアンモニア注入量を制御しなければならないこと、一般に装置が大型となること等の問題点がある。

【０００６】また、別な方法として、水素、一酸化炭素、炭化水素等のガスを還元剤として用い、窒素酸化物を還元する非選択的接触還元法があるが、この方法では、効果的な窒素酸化物の低減除去を実行するためには排ガス中の酸素との理論反応量以上の還元剤を添加しなければならず、還元剤を多量に消費する欠点がある。このため非選択的接触還元法は、実際上は、理論空燃比付近で燃焼した残存酸素濃度の低い排ガスに対してのみ有効となり、汎用性に乏しく実際的でない。

【０００７】そこで、ゼオライト又はそれに遷移金属を担持した触媒を用いて、排ガス中の酸素との理論反応量以下の還元剤を添加して窒素酸化物を除去する方法が提案された（たとえば、特開昭63-100919 号、同63-283727 号、特開平1-130735号、及び日本化学会第59春季年会（1990年)2A526、同第60秋季年会（1990年)3L420、3L422 、3L423 、「触媒」vol.33 No.2 、59ページ、1991年等）。

【０００８】しかしながら、これらの方法では、水分を含まないような模擬排ガスに対しては高い効率で窒素酸化物を除去することはできるが、実際の排ガスでは水分を１０％程度含有するので、窒素酸化物の除去率が著しく低下することがわかった。

【０００９】したがって、本発明の目的は、固定燃焼装置および酸素過剰条件で燃焼するガソリンエンジン、デ

ィーゼルエンジン等からの燃焼排ガスのように、窒素酸化物、一酸化炭素、炭化水素等の未燃焼分に対する理論反応量以上の酸素を含有する燃焼排ガスから、効率良く窒素酸化物を除去することができる窒素酸化物触媒及びそれを用いた方法を提供することである。

【００１０】

【課題を解決するための手段】上記課題に鑑み鋭意研究の結果、本発明者は、排ガスに含まれる窒素酸化物の量に見合った量の炭化水素又は含酸素有機化合物を添加した排ガスを、多孔質の無機酸化物に特定量の(a) 銀又は銀酸化物と(b) アルカリ金属またはアルカリ土類金属とを担持してなる触媒に特定の温度で接触させれば、窒素酸化物を効果的に除去することができることを発見し、本発明を完成した。

【００１１】すなわち、窒素酸化物と、共存する未燃焼成分に対する理論反応量より多い酸素とを含む燃焼排ガスから窒素酸化物を除去する本発明の触媒は、多孔質の無機酸化物１００重量％に、(a) 銀又は銀酸化物を０．２～１５重量％（銀元素換算値）と、(b) アルカリ金属元素とアルカリ土類金属とからなる群より選ばれた少なくとも一種の金属元素を銀成分担持量の５０重量％以下（金属元素換算値）担持してなり、前記触媒を排ガス導管の途中に設置し、前記触媒の上流側で前記排ガス中の窒素酸化物重量の５倍以下の炭化水素又は含酸素有機化合物を添加し、２００～６００℃において排ガスが前記触媒に接触し、もって、前記炭化水素又は含酸素有機化合物との反応により前記窒素酸化物を除去することを特徴とする。

【００１２】また、窒素酸化物と、共存する未燃焼成分に対する理論反応量より多い酸素とを含む燃焼排ガスから窒素酸化物を除去する本発明の第一の方法は、多孔質の無機酸化物１００重量％に、(a) 銀又は銀酸化物を０．２～１５重量％（銀元素換算値）と、(b) アルカリ金属元素とアルカリ土類金属とからなる群より選ばれた少なくとも一種の金属元素を銀成分担持量の５０重量％以下（金属元素換算値）担持してなる触媒を排ガス導管の途中に設置し、前記触媒の上流側に、前記排ガス中の窒素酸化物重量の５倍以下の炭化水素又は含酸素有機化合物を添加し、２００～６００℃において排ガスを前記触媒に接触させ、もって、前記窒素酸化物と前記炭化水素又は含酸素有機化合物とを反応させて前記窒素酸化物を除去することを特徴とする。

【００１３】さらに、窒素酸化物と、共存する未燃焼成分に対する理論反応量より多い酸素とを含む燃焼排ガスから窒素酸化物を除去する本発明の第二の方法は、多孔質の無機酸化物１００重量％に、(a) 銀又は銀酸化物を０．２～１５重量％（銀元素換算値）と、(b) アルカリ金属元素とアルカリ土類金属とからなる群より選ばれた少なくとも一種の金属元素を銀成分担持量の５０重量％以下（金属元素換算値）担持してなる触媒を排ガス導管の途中に設置し、２００～６００℃において排ガスを前記触媒に接触させ、もって、前記窒素酸化物と前記排ガス中の残留炭化水素とを反応させて前記窒素酸化物を除去することを特徴とする。

【００１４】以下、本発明を詳細に説明する。本発明で用いる触媒は、多孔質の無機酸化物に(a) 銀又は銀酸化物と、(b) アルカリ金属元素とアルカリ土類金属とからなる群より選ばれた少なくとも一種の金属元素とを担持してなる。

【００１５】まず、多孔質の無機酸化物としては、多孔質のアルミナ、チタニア、ジルコニア、及びそれらの複合酸化物等を使用することができるが、好ましくはγ－アルミナ又はアルミナ系複合酸化物を用いる。

【００１６】多孔質の無機酸化物の比表面積は３０m^2／g以上であるのが好ましい。比表面積が３０m^2／g未満であると、排ガスと無機酸化物との接触面積が小さくなり、良好な窒素酸化物の除去が行えない。多孔質無機酸化物のより好ましい比表面積は８０m^2／g以上とする。特に１００m^2／g以上が好ましい。

【００１７】γ－アルミナ等の無機酸化物には後述するように銀又は銀酸化物とアルカリ金属、アルカリ土類金属とが担持されるが、この無機酸化物は、ペレット状、粉末状、ハニカム状、フォーム状、板状等の状態で用いることができる。また、耐熱性のコージェライト、ムライト等の成分からなるハムニカ状、フォーム状の基体に活性種を担持した多孔質無機酸化物をコートして用いることもできる。本発明の触媒の好ましい形態はセラミックス製又は金属製の基体表面に触媒をコートして用いる。本発明の触媒のもう一つ好ましい形態はペレット状の多孔質無機酸化物に触媒活性種を担持して用いる。

【００１８】本発明では、上述したγ－アルミナ等の無機酸化物に（ａ）銀又は銀酸化物と、（ｂ）アルカリ金属元素、アルカリ土類金属からなる群より選ばれた少なくとも一種の金属元素とを担持したものを触媒として用いる。銀又は銀酸化物の担持量は、排ガス中に添加するガス状の炭化水素又は含酸素有機化合物の種類、排ガスとの接触時間などによって多少変化するが、無機酸化物を100 重量％として、その0.2 ～15重量％（銀元素換算値）とする。0.2 重量％未満では、銀又は銀酸化物の担持による効果が顕著とはならず、また15重量％を超す量の銀又は銀酸化物を担持しても、NOx の除去性能の向上はみられない。好ましい銀又は銀酸化物の担持量は0.5 ～10重量％である。なお、無機酸化物に担持された銀は、排ガスの温度領域では金属又は酸化物の状態にあり、相互に容易に変換し得る。

【００１９】アルカリ金属としては、セシウム、ナトリウム、カリウムなどを用いるのが好ましい。また、アルカリ土類金属としては、カルシウム、ストロンチウム、バリウムを用いるのが好ましい。

【００２０】アルカリ金属元素、アルカリ土類金属の合

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計担持量は銀成分を100 重量％として、５０重量％以下（元素換算値）とする。担持量が銀成分の５０重量％を超えると銀成分による除去効果が大きく低下する。なお、担持量の下限値を0.001 重量％とするのが好ましい。なお、上記金属は、排ガスの温度領域では酸化物の状態で存在する。

【００２１】γ－アルミナ等の無機酸化物に銀やアルカリ金属元素、アルカリ土類金属を担持する方法としては、公知の浸漬法等を用いることができる。その際、硝酸塩水溶液等に多孔質の無機酸化物を浸漬し、７０℃程度で乾燥後、１００～６００℃で段階的に昇温して焼成するのが好ましい。焼成は、酸素雰囲気、窒素雰囲気下や水素ガス流下で行うのが好ましい。窒素雰囲気下や水素ガス流下で行う場合では、最後に酸化処理を行う。これにより銀のシンタリングを防止し、窒素酸化物の浄化特性の低下を防ぐ。

【００２２】次に、本発明の方法について説明する。排ガス中には、残留炭化水素としてエチレン、プロピレンなどがある程度含まれる。残留炭化水素が排ガス中の窒素酸化物を還元するのに十分でない場合には、外部から有機化合物を添加する必要がある。このとき、上述した触媒を排ガス導管の途中に設置し、触媒の設置部位の上流側で排ガス中に炭化水素又は含酸素有機化合物を添加する。

【００２３】炭化水素としては、アルカン、アルケン、アルキン、灯油、軽油等を用いる。好ましくは、アセチレンや、炭素数３以上のアルケン（たとえばプロピレン）、灯油、軽油などの液状炭化水素等を用いる。含酸素有機化合物としては、エタノール等のアルコール類を用いるのが好ましい。

【００２４】排ガス中に添加する炭化水素又は含酸素有機化合物の量は、排ガス中の窒素酸化物の重量の５倍以下とする。５倍を超すと、添加物が過剰となる場合が多く、未反応の炭化水素又は含酸素有機化合物が排ガス中に残る可能性が高い。好ましくは添加量を窒素酸化物量の３倍以下とする。なお、排ガス中には、未燃焼分としてアルカン、アルケン、アルキン等の炭化水素が多少存在するので、上述した触媒を用いただけでも（炭化水素を添加しなくとも）、ある程度のNOx の低減効果がみられる。

【００２５】また、本発明では、触媒設置部位における排ガスの温度を２００～６００℃に保つ。排ガスの温度が２００℃未満であると添加物と窒素酸化物との反応が進行せず、良好な窒素酸化物の除去を行うことができない。一方、６００℃を超す温度とすると、添加される有機物が燃焼し、窒素酸化物の還元除去特性は大きく低下する。

【００２６】一般に、接触時間が短くなると窒素酸化物の除去特性は低下する。したがって、接触時間が短いときは触媒活性種の担持量を多く、また接触時間が長いときは触媒活性種の担持量を少なめに担持するのが好ましく、このようにすると、炭化水素と窒素酸化物との反応を効率良く進行させることができる。本発明における触媒では、排ガスを上記の触媒に接触させる接触時間を０．００６秒・ｇ／ml以上とするのが好ましい。ここで、接触時間は、炭化水素を含有する排ガス１ml（ただし標準状態に換算した体積）が１ｇの触媒と接触する時間（秒）を表している。好ましい接触時間は０．００７秒・ｇ／ml以上とする。

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【００２７】

【実施例】本発明を以下の具体的実施例によりさらに詳細に説明する。

実施例１

市販のペレット状の多孔質γ－アルミナ（各々直径１．５mm、長さ約６mm、比表面積200 m^2 ／ｇ）１０ｇを硝酸銀と硝酸カリウムの混合水溶液に浸漬し、７０℃で乾燥後、５容量％の水素を含む窒素気流下で、１５０℃、２００℃、３００℃、４００℃、５００℃及び６００℃の各温度でそれぞれ２時間焼成し、ペレット状γ－アルミナに対して銀２重量％（元素換算値）、及びカリウム０．５重量％（元素換算値）を担持した。

【００２８】次に、得られた触媒３．６ｇを反応管内に設置し、表１に示す組成のガス（一酸化窒素、酸素、プロピレン、及び窒素）を毎分４．４リットル（標準状態）の流量で流して（このとき、空間速度は30000 h^{-1} であり、接触時間は0.05秒・ｇ／mlであった）、反応管内の排ガス温度を３００～６００℃の範囲に保ち、プロピレンと窒素酸化物とを反応させた。

【００２９】反応管通過後のガス中の窒素酸化物の濃度を化学発光式窒素酸化物分析計により測定し、窒素酸化物の除去率を求めた。結果を図１に示す。

【００３０】表１

成分	濃度
一酸化窒素	800 ppm
酸素	10 容量％
プロピレン	1714ppm
窒素	残部

【００３１】実施例２

実施例１と同様の方法で、粉末状γ－アルミナ（平均粒径４０μm、比表面積２００m^2 ／ｇ）に銀２重量％（元素換算値）、及びカリウム０．５重量％（元素換算値）を担持した触媒１．３ｇを、市販のコージェライト製ハニカム成形体（直径３０mm、長さ１２．５mm）にウォッシュコート法によりコートした。この触媒をコートした成形体を用い、実施例１と同様の条件（空間速度は３００００h^{-1}）で、窒素酸化物の除去試験を行った。試験結果を図１に示す。

【００３２】比較例１

実施例１と同様の方法で、γ－アルミナペレットに銀のみを２重量％担持して触媒とした。この触媒を用い、反

応管内の排ガス温度を３００～６００℃の範囲に保った以外は実施例１と同様にして、窒素酸化物の除去試験を行った。試験結果を図１に示す。

【００３３】比較例２

実施例１と同様の方法で、γ－アルミナペレットに銀を２重量%、Ｃｅを０．５重量%担持して触媒とした。この触媒を用い、実施例１と同様にして窒素酸化物の除去試験を行った。結果を図１に示す。

【００３４】以上からわかるように、実施例１、２においては、特に４００～６００℃の排ガス温度で窒素酸化物の良好な除去がみられた。一方、アルカリ金属を担持しない銀成分のみの触媒を用いると（比較例１）、５００℃での窒素酸化物の除去率が低くなる。また、銀成分と希土類金属とを担持した触媒（比較例２）において、全温度範囲内で高い窒素酸化物の除去が得られなかった。

【００３５】

【発明の効果】以上詳述したように、本発明の触媒及び方法によれば、過剰の酸素を含む排ガス中の窒素酸化物を効率良く除去することができる。窒素酸化物の除去温度（排ガス温度）も５００℃程度以下と、これまでの除去方法に比して低温で行うことができる。

【００３６】本発明の窒素酸化物除去触媒及び方法は、各種燃焼機、自動車等の排ガスに含まれる窒素酸化物の除去に広く利用することができる。

【図面の簡単な説明】

【図１】実施例１、２及び比較例１、２における排ガス温度と窒素酸化物の除去率との関係を示すグラフである。

【図１】